Comment to the EPA regarding the proposed cleanup plan for the Olin Chemical Superfund Site in Wilmington, MA

The Massachusetts Institute of Technology Superfund Research Program (MIT SRP) appreciates the opportunity to provide feedback regarding the EPA's plan for remediating the Olin Chemical Superfund site, proposed in August 2020. Here, we have integrated expertise from our chemists, environmental engineers, and biologists in consideration of the proposed plan.

DAPL interim action

We are pleased that there are proposed interim actions to remediating the dense aqueous phase liquid (DAPL) pool. Given the complexity of the environmental contamination and potential for continued plume expansion and human exposure, interim action is appropriate. We agree that continued quarterly monitoring of the 18 currently tested wells for nitrosamine contamination is appropriate, but this should be expanded to include other nitrosamines and contaminants beyond *N*-nitrosodimethylamine (NDMA) only. In addition, we feel it is extremely important to characterize the full chemical composition of DAPL in order to understand the health risks to the community, past, present, and future.

One specific concern is the proposed method of "pump-and-treat" for DAPL. Historically, pump-and-treat is ineffective because the entire mass cannot be treated simultaneously, and turnover rates are extremely slow relative to the size and dynamics of the plume. Even if DAPL is treated effectively, upon reinjection it returns to the contaminated plume and facilitates plume migration, and it may still contain precursors that re-form hazardous chemicals. Treated waste must be tested for any potentially hazardous contents before re-release into any environment. As one example, the pump and treat method for remediating trichloroethylene on Cape Cod ultimately has not served to reduce contamination. We encourage the EPA to provide evidence of efficacious pumping and treatment in similar contexts before this method is applied to DAPL.

LNAPL and soil/sediment actions and ongoing nitrosamine formation

The proposed final actions regarding the light non-aqueous phase liquid (LNAPL) and soil/sediment are not satisfactory to our technical experts. As with the DAPL, we are concerned about the efficacy of pumping and treatment for LNAPL. Considering the history of chemical disposal at the site, NDMA precursors and other chemical hazards are likely present in the LNAPL and soil/sediment, and more aggressive assessment and response (e.g., excavation and/or containment) is necessary. Olin manufactured nitrosamine products, namely *N*-nitrosodiphenylamine (aka. Wiltrol N, discussed further below) and a product called "Opex" (dinitrosopentamethylenetetramine), which may be less mobile in the environment than NDMA due to soil sorption, thus necessitating more aggressive soil remediation. The acidity of the site's waste, combined with these manufactured nitrosamines, may create conditions favoring ongoing

formation of more mobile nitrosamines (like NDMA) via trans-nitrosation that could continue to leach into the groundwater.

Additionally, numerous nitrosamine precursors or materials known to create nitrosamine-forming conditions are known or highly likely to be present in the LNAPL and soil/sediment, including: hydrazines (which were manufactured at this site); raw materials for Nitropore 5PT (a product formerly manufactured at this site); aqueous ammonia and chlorine (known contaminants in high levels). Organic hydrazine derivatives are well-established precursors for *N*-nitrosamines, but Olin has been vague about their hydrazine manufacturing conditions and methods for treatment and disposal. Nitropore 5PT (aka Expandex 5 PT, 5-phenyltetrazole) manufacturing utilized sodium nitrite, dimethylformamide (DMF), and strong acid; similar conditions were recently found to be the source of NDMA contamination in the blood pressure medication Valsartan, leading to unacceptable levels of human exposure and prompting recall of the drug. Aqueous ammonia and chlorine, which react to form chloramines, are found at concerningly high levels in both surface and groundwater. Chloramines have long been known to produce nitrosamines from reaction with a wide variety of precursors. All of these chemicals are mobile in the environment and continue to contaminate the site; it is therefore reasonable to expect that these precursors will continue to react and form toxic and carcinogenic *N*-nitrosamines, including NDMA. Over time, this novel formation will reduce the efficacy of efforts to remediate the DAPL and restore the environment of Wilmington. Further, because the slurry wall was not installed to bedrock and leaves opportunity for fluid transport, ongoing NDMA production would continue to contaminate the groundwater of Wilmington until these chemical sources are removed and an effective barrier constructed.

Other nitrosamines (besides NDMA) are important

In addition to our concerns about the proposed remedial actions, we would like to call attention to the importance of monitoring additional nitrosamines in the environment. *N*-nitrosamines, a class comprising hundreds of chemicals, are among the most potent carcinogens known. Over 70 *N*-nitrosamines have been documented to cause cancer in animals, and most of them are not currently tested for at the Olin site. For example, *N*-nitrosodiethylamine (NDEA) is even more toxic and carcinogenic than NDMA, and given its structural similarity, it is almost certainly present at the site, but it does not appear to be routinely measured (Nobis OU3 RI report 2019).

One nitrosamine that contaminates the site and should be a substantial concern is *N*-nitrosodiphenylamine (NDPhA) (not to be confused with *N*-nitrosodi-*n*-propylamine, NDPA. Notably, the abbreviation NDPA is used interchangeably for the propyl and phenyl compounds in many reports). NDPhA was manufactured at the site and has been found in the Olin site LNAPL and groundwater. Although NDPhA does not directly damage DNA (whereas NDPA does), it is an EPA class B2 probable carcinogen, and it is a precursor for NDMA (McGregor 1994, *Mutation Research*). Given the relative thermal instability and low volatility of NDPhA,

GC/MS (or GC/MS/MS) analysis of this chemical is problematic – NDPhA is expected to decompose at the elevated temperatures required for this approach. Thus, results of NDPhA testing at Olin likely underestimate the true level of contamination. Even so, NDPhA has been found at unacceptably high levels (see EPA/Nobis Engineering letter of disapproval March 2018 RI/FS Deliverables). Given the known contamination of the site with additional nitrosamines, and the potential for even more toxic nitrosamines, it is important to take measures in identifying, monitoring, and remediating other nitrosamines in DAPL, LNAPL, and groundwater.

We appreciate the careful consideration of our concerns by the EPA, MassDEP, and Olin, and we look forward to an improved cleanup proposal following this public comment period.

These comments are from Dr. Jenny Kay, Dr. Kathy Vandiver, Ms. Jessica Beard, Prof. Bevin Engelward, and Prof. Timothy Swager, on behalf of the MIT Superfund Research Program.